FCCU Regenerator Lab-Scale Simulator for Testing New Catalytic Additives for Reduction of Emissions from the FCC Regenerator

George Yaluris, Xinjin Zhao, Alan W. Peters
W. R. Grace & Co.-Conn.
Washington Research Center
7500 Grace Dr., Columbia, MD 21044

Keywords: Fluid catalytic cracking unit (FCCU) regenerator lab-scale simulator, combustion promoter, NO_x reduction

Introduction

Catalyst additives are commonly used in the FCC regenerator to control CO, SO_x and NO_x emissions (1). For example, Pt based combustion promoters are typically used to reduce CO emissions. The development of DESOX® technology has provided refiners with catalyst additives that can reduce the SO_x emissions (2-4). Recent environmental regulations have increased the importance of such catalyst additives in the FCC process and the need to develop new FCCU regenerator additives (5). Due to the lack of a realistic lab-scale simulator of the FCCU regenerator, most of the work in developing catalyst additives for the regenerator has been conducted using either refinery FCC units or pilot plants (e.g., Davison Circulating Riser (DCR), an adiabatic riser with continuous catalyst regeneration) (6,7). The efforts to develop new catalyst additives can be facilitated by the development of a lab-scale unit that simulates the FCCU regenerator. This simulator would allow us to examine the regenerator chemistry and the mechanisms through which additives affect gas emissions, as well as routinely test new additives. In this paper we present the development of such a lab-scale simulator of the FCCU regenerator and its use in testing combustion promoter additives.

Lab-Scale Simulator Unit of FCCU Regenerator

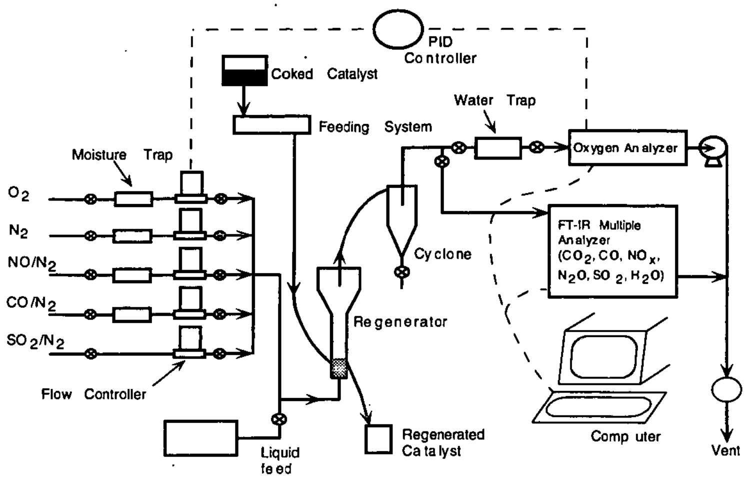
Attempting to simulate all of the operational characteristics of refinery-scale regenerators, which vary significantly in design, in a small lab-scale unit is not practical. For example, it is difficult to simulate the catalyst and gas flow patterns of a large regenerator in an idealized lab-scale reactor, and to simulate the true condition of the catalyst and additives entering the regenerator from the stripper. Thus, we have designed a one-pass system that utilizes pre-coked catalyst, operates as close as possible to the operation conditions of refinery regenerators, captures the chemical phenomena occurring in a true regenerator, and predicts the performance of catalyst additives.

The main characteristics of the lab-scale simulator unit of the FCCU regenerator (FCCU-RSU) are:

1. Fluidization of the FCC catalyst and additives
2. Continuous coked catalyst flow through the reactor and ability to control the catalyst residence time in the reactor
3. Control of the excess oxygen in the reactor effluent
4. Control of the temperature of the exothermic coke burning reaction
5. Ability to conduct mechanistic and kinetic experiments to probe the regenerator chemistry (formation of CO, SO_x and NO_x) and the mechanism through which catalyst additives work

In Figure 1 we show a schematic diagram of the FCCU-RSU we have built. The system consists of a quartz glass tube reactor (2.54 cm diameter) with a gas-catalyst particles disengagement section at the top. Further, separation of catalyst fines is achieved in the cyclone that follows the reactor. A custom designed oven allows control of the reactor temperature during the fast exothermic coke burning reaction. Air, oxygen, nitrogen, CO, NO, SO_2, and evaporated liquid feed can be fed in the reactor. Typically, nitrogen is used to fluidize the catalyst bed. Emission gases, like CO, NO and SO_2, are used in kinetic and mechanistic experiments to study the interactions between these gases, the catalyst, and the additives. A

Figure 1: Schematic diagram of FCCU regenerator lab-scale simulation.



portion of the reactor effluent is sent to a Horiba oxygen analyzer (MPA-510), and through a feedback loop a PID controller controls the amount of air or oxygen needed to maintain the desired excess oxygen in the effluent. All other reactor gas products are analyzed by an On-Line Technologies 2002 FTIR Multigas analyzer which can measure CO_2, CO, NO, N_2O, NO_2, SO_2, H_2O and other FTIR-active gases. The catalyst flows continuously through the reactor using a custom-designed catalyst flow system purged with nitrogen to avoid contamination of reaction products with atmospheric gases. The catalyst residence time in the reactor depends on the catalyst flow rate, and can be controlled from about 5 min to more than 2 h. Detailed mixing experiments showed that mixing in the reactor is close to that of a CSTR.

Experimental

Using the FCCU-RSU we studied the performance of conventional Pt-based CO combustion promoters as well as that of new non-conventional additives that combine the CO combustion promotion functionality with reduction of NO_x from the regenerator (XNOx™ additives). The additives were used in our studies as synthesized both after calcination in air at 773 K and after reduction at 773 K in flowing 4% H_2 in N_2. Commercial FCC catalysts were coked in our pilot plant (DCR) using a resid FCC feed (API @ 60 °F: 20.6) that contains 0.41% sulfur, 0.18% total nitrogen, 0.06% basic nitrogen, and 5.1% Conradson carbon. The coked catalysts contained *ca.* 0.9 - 2.5% coke. The additives were added to the catalyst at the level of 0.5 wt%. Before charging the catalyst to the catalyst feed system, the catalyst was dried overnight at 373 K.

Typically the catalyst residence time in the reactor was about 16 min, and the excess oxygen was controlled at 1.1%. Unless otherwise noted, the reaction temperature was varied from 973 K to 1003 K. Data was collected for 30 - 60 min after steady state had been achieved.

Results

The results of coked catalyst regeneration in the FCCU-RSU show that the unit simulates well the catalyst regeneration process in the refinery regenerator. The CO/CO_2 ratio is a strong function of temperature and excess oxygen and decreases with increasing temperature and increasing excess oxygen. In Figure 2 we show that the amounts of CO detected in the flue gas follow inversely the amount of excess oxygen. At 1043 K, CO_2 increases from 1.6% to 3.0% to 4.4% as the catalyst flow increases from 0.47 to 1.07 to 1.67 g/min. Figure 2 shows that as the catalyst flow increases (catalyst residence time decreases) the amount of SO_2 increases roughly proportional to the increase in catalyst flow. These results are an

Figure 2: Composition of reactor effluent gas during regeneration of an FCC catalyst containing about 2.5% coke. CO, NO, SO_2 in ppm. Excess O_2 in %. Reactor temperature 1043 K.

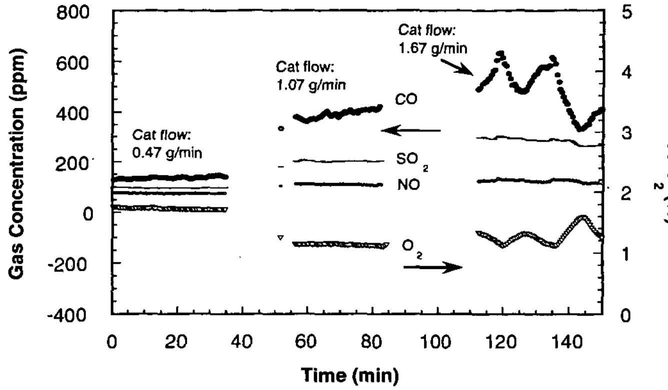
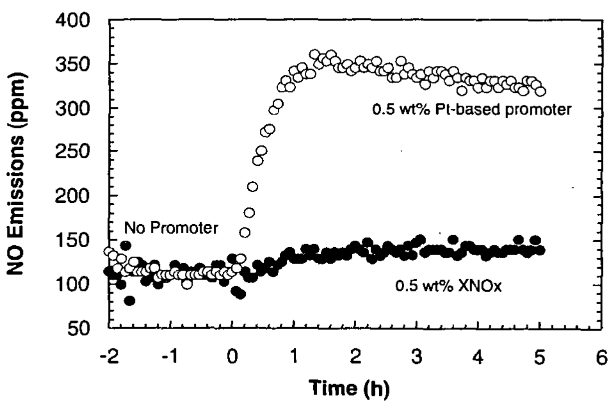


Figure 3: NO emissions from the pilot plant (DCR) regenerator when Pt-based and XNOx™-based combustion promoters are added in the catalyst (at 0 h)at 0.5 wt% additive level. Typical DCR regenerator temperature is 977 K.



indication that at the temperature of this experiment most combustion of coke occurs during the first few minutes of the catalyst residence time in the regenerator. CO also increases with decreasing catalyst residence time, but its concentration in the flue gas depends on oxygen flow as well. NO increases as more coked catalyst is fed to the reactor. However, because of its reaction with CO, it does not increase in proportion to the catalyst flow increase.

According to refinery as well as our pilot plant experience (8), when Pt-based combustion promoters are added in the regenerator to reduce CO emissions, NO_x emissions increase. In DCR testing (Figure 3), the addition of Pt-based promoter in the regenerator increased NO formation during the cracking of a light paraffinic feed by about 3 times. In agreement with these results, the FCCU-RSU also shows a dramatic increase of NO_x in the reactor effluent when a Pt-based combustion promoter is added to the coked catalyst at the level of 0.5 wt%. The magnitude of the increase in the amount of nitrogen oxides produced depends on the reactor temperature and can be as high as five fold (Table 1)

Recently we developed new combustion promoter technology (8) that can achieve similar reduction of CO emissions from the FCCU regenerator as can be

Table 1: Average amounts of gas formation during FCC coked catalyst regeneration (1.2 wt% coke) with or without combustion promoter additives. Values shown are in cc/g catalyst passed through the reactor, averaged over 30 - 60 min after the unit has achieved steady state.

Promoter	Nominal Bed Temp (K)	CO_2	CO	N_2O	NO	SO_2	Nitrogen Oxides (%) Change	Effect on CO (%) Change
None	973	11.7	9.74	0.008	0.039	0.080	0	0
Pt-based oxid.	973	18.9	1.59	0.003	0.251	0.061	435	84
Pt-based red.	973	18.0	1.36	0.002	0.245	0.056	420	86
XNOx™ oxid.	973	17.2	2.45	0.004	0.169	0.021	264	75
XNOx™ red.	973	18.0	2.52	0.003	0.173	0.020	270	74
None	988	18.2	3.75	0.031	0.065	0.086	0	0
Pt-based oxid.	988	19.7	1.51	0.005	0.255	0.066	171	60
Pt-based red.	988	20.7	1.41	0	0.260	0.067	172	62
XNOx™ oxid.	988	19.5	1.83	0.008	0.188	0.027	105	51
XNOx™ red.	988	19.9	1.95	0.008	0.186	0.025	103	48

achieved with Pt-based promoters, while it produces a significantly smaller increase in NO_x emissions. We tested in the DCR a non-conventional combustion promoter based on XNOx™ technology (Figure 3). With the new combustion promoter in the DCR regenerator, NO emissions increased only 20%. The lab-scale simulator of the FCC regenerator qualitatively gives the same performance results. When XNOx™ is added to the coked catalyst at 0.5 wt%, nitrogen oxides in the flue gas increase about 40% less than the increase measured for the Pt-based additive (Table 1).

The observed reduction in nitrogen oxide emissions is achieved at only a slight cost in CO combustion promotion (Table 1). When the formulation of the XNOx™ combustion promoter is adjusted to achieve the same combustion promotion as the Pt-based additive, the FCCU-RSU still shows that, compared to the Pt-based additive, the XNOx™ additive achieves similar decreases in the concentration of nitrogen oxides in the reactor effluent to those shown in Table 1. Thus, the reduced NO_x achieved with the use of XNOx™ combustion promoters is a result of the additive's unique chemistry and not due to an increase of the CO reaction with NO that may result from the small increase of CO in the reactor. It is worth noting that according to the data in Table 1, significant amounts of N_2O are formed only in the absence of combustion promoters. Apparently, when these additives are present in the reactor, N_2O is rapidly oxidized to NO.

In an FCCU, the combustion promoters enter the regenerator after being reduced in the riser. To determine if the oxidation state of the additive affect its performance, we tested both oxidized and reduced additives. Our results (Table 1), indicate that, at least in the FCCU-RSU, the oxidation state of the additive does not have a significant impact on either the CO combustion promotion or the observed increase in NO_x. This result does not imply that the redox properties of the additive do not impact the flue gas composition. We speculate that upon entering the reactor, at the conditions of these experiments (>973 K, >1% O_2, and CO present), the additive rapidly reaches its equilibrium oxidation state. The presence of redox catalytic cycles involving surface sites and O_2, CO, NO and other nitrogen species may then play a role in determining the amount of nitrogen oxides produced during catalyst regeneration.

Conclusions

We have developed a lab-scale simulator of the FCCU regenerator that can be used to study the performance of FCC regenerator catalyst additives, and investigate the mechanism (e.g., role of additive's oxidation state) and kinetics through which these additives affect the formation of carbon, nitrogen and sulfur oxides. The lab-scale system includes a custom-designed fluidized bed reactor and catalyst flow system, and allows control of the important operation parameters (catalyst residence time, excess oxygen, reactor temperature). Coked catalyst regeneration experiments and performance tests of conventional and non-conventional combustion promoters show that the FCCU-RSU can simulate the operation and capture the chemistry of the FCCU regenerator.

References:

1. Bhattacharyya, A.A., and Yoo, J.S. *in* "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf. Sci. Catal.* Vol. 76, p. 531 . Elsevier Science Publishers B. V., Amsterdam, 1993.
2. Lane, P.A., and Latimer, J.A. *in* "Advanced Fluid Catalytic Cracking Technology" (Chuang, K.C., Young, G.W. and Benslay, R.M. Eds.), *AIChE Symp. Ser., No. 291* Vol. 88, p. 76. American Institute of Chemical Engineers, New York, 1992.
3. Yoo, J.S.,Karch, J.A.,Radlowski, C.A., and Bhattacharyya, A.A. *in* "Catal. Sci. Technol., Proc.," Tokyo, 1990, (Yoshida, S., Takezawa, N. and Ono, T. Eds.), , p. 183. Kodansha , Tokyo, 1991.
4. Yoo, J.S.,Bhattacharyya, A.A.,Radlowski, C.A., and Karch, J.A., *Appl. Catal., B* **1(3)**, 169 (1992).
5. Evans, R.E., and Quinn, G.P. *in* "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf. Sci. Catal.* Vol. 76, p. 563. Elsevier Science Publishers B. V., Amsterdam, 1993.
6. Peters, A.W.,Weatherbee, G.D., and Zhao, X., *Fuel Reformulation* **5(3)**, 45 (1995).
7. Young, G.W. *in* "Fluid Catalytic Cracking: Science and Technology" (Magee, J.S. and Mitchell, M.M., Jr. Eds.), *Stud. Surf. Sci. Catal.* Vol. 76, p. 257 . Elsevier Science Publishers B. V., Amsterdam, 1993.
8. Davey, S.W., and Haley, J.T. *in* "Oil & Gas Journal International Catalyst Conference and Exhibition," Houston, Texas, February 1-2, 1996.